April 2003 • NREL/CP-520-33936

Conference Paper

Influence of Filament and Substrate Temperatures on Structural and Optoelectronic Properties of Narrow Gap a-SiGe:H Alloys Deposited by Hot-Wire CVD

Preprint

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To be presented at the 2003 Materials Research Society Spring Meeting
San Francisco, California
21-25 April 2003

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

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Contract No. DE-AC36-99-GO10337

Influence of Filament and Substrate Temperatures on Structural and Optoelectronic Properties of Narrow Gap a-SiGe:H Alloys Deposited by Hot-Wire CVD

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ABSTRACT

We have found that narrow-bandgap—1.25 < Tauc Gap < 1.50 eV—amorphous silicon germanium (a-SiGe:H) alloys grown by hot-wire chemical vapor deposition (hot-wire CVD) can be improved by lowering both substrate and filament temperatures. We systematically study films deposited using a one-tungsten filament, decreasing filament temperature (T_f) from our standard temperature of 2150° down to 1750°C, and fixing all other deposition parameters. By decreasing T_f at the fixed substrate temperature (T_s) of 180°C, the Ge-H bonding increases, whereas the Si-H_2 bonding is eliminated. Films with higher Ge-H bonding and less Si-H_2 have improved photoconductivity. For the series of films deposited using the same germane gas fraction at 35%, the energy where the optical absorption is $1x10^4$ (E04) drops from 1.54 to 1.41 eV with decreasing T_f. This is mainly due to the combination of an increasing Ge solid fraction (x) in the film, and an improved homogeneity and compactness due to significant reduction of microvoids, which was confirmed by small angle X-ray scattering (SAXS). We also studied a series of films grown by decreasing the T_s from our previous standard temperature of 350°C down to 125°C, fixing all other deposition parameters including T_f at 1800°C. By decreasing T_s, both the total hydrogen content (C_H) and the Ge-H bonding increased, but the Si-H_2 bonding is not measurable in the T_s range of 180°-300°C. The E04 increases from 1.40 to 1.51 eV as T_s decreased from 350° to 125°C, mainly due to the increased total hydrogen content (C_H). At the same time, the photo-to-dark conductivity ratio increases almost three orders of magnitude over this range of T_s.

INTRODUCTION

We first reported at the 1998 MRS Spring Conference that we can deposit high-quality a-SiGe:H alloys with bandgaps over 1.5 eV at high deposition rates over 10 Å/s by hot-wire CVD[1]. We then fabricated a-Si:H/a-SiGe:H tandem solar cells using these mid-gap a-SiGe:H alloys and obtained a conversion efficiency over 11% [2]. In the earlier papers, we showed that substrate temperatures over 270°C produced high-quality mid-gap materials. However for a-SiGe:H alloys below 1.5 eV (which we call narrow gap), we observed that high T_s and high T_f were deleterious to the film quality. Therefore, recently we focused our research on this narrow-bandgap region, 1.25 eV< Tauc Gap (E_{Tauc}) < 1.50 eV, in different process regimes than used for our mid-gap materials [3, 4]. In this paper, we present the effect of T_f and T_s on the structural and optoelectronic properties of a-SiGe:H films grown by hot-wire CVD.

EXPERIMENTAL DETAILS

We deposited two sets of films. The first set was deposited by reducing T_f from 2150°C to 1750°C with all other deposition parameters were fixed. The second set was deposited by reducing T_s from 350°C to 125°C with all other deposition parameters fixed. See Table 1 for a list of select deposition parameters, the film thicknesses and deposition rates (D.R.) for the films examined in this paper.

Table 1. Deposition Parameters of the Samples*.

Sample (Set 1)	T_f (°C)	T_s (start) (°C)	Thick. (Å)	D. R. (Å/s)	Sample (Set 2)	T_s (°C)	T_f (start) (°C)	Thick. (Å)	D. R. (Å/s)
L902	2150	180	2976	9.92	L908	350	1800	2919	3.04
L904	2065	180	3434	8.18	L894	300	1800	4087	3.45
L905	1975	180	3315	6.50	L895	250	1800	3669	3.08
L907	1880	180	2997	4.16	L896	200	1800	3622	2.92
L911	1800	180	2128	2.03	L897	150	1800	3501	2.84
L913	1750	180	2085	0.98	L898	125	1800	2856	2.14

* All samples are deposited using the same GeH_4 gas ratio of GeH_4 /(GeH_4+SiH_4) =35%, the same H_2 dilution ratio of H_2/(GeH_4+SiH_4) = 1, and at the same deposition pressure of 15 mTorr.

The hot wire deposition chamber used in this study is a 10-cm-diameter × 30-cm-long stainless steel tube mounted inside of a standard high-vacuum 6-way cross [3]. The outside of this tube is wrapped with an encapsulated resistive heater in a pattern that provides an isothermal region in the center of the tube, the location of the substrate during deposition. The filament used in this study is one tungsten wire 0.38 mm in diameter and about 22 cm in straight length and 18 cm in coiled length. The spacing from the filament to substrate is 5 cm, and the T_f is calculated from tables listing the filament diameter and current, and is also calibrated by a two-wavelength pyrometer under vacuum conditions.

We deposited a-SiGe:H films simultaneously on 1737F Corning glass and c-Si wafers. We evaporated coplanar (width to length = 0.05) Cr contacts on the films on the 1737F substrates for conductivity measurements. We also performed optical measurements using an n&k 1280 analyzer on the films grown on 1737F substrates to determine the thickness (Å), bandgap (E04), which is the photon energy where the optical absorption is $1x10^4$. The Tauc bandgap is taken from the fitting of E vs. $(\alpha h\upsilon)^{1/2}$, in which α is calculated by the method of interference-free determination of optical absorption coefficient [5] on the raw transmission and reflectance data.

The FTIR absorption spectra were obtained from the films deposited on c-Si wafers by a Nicolet 510 system between 400 and 4000 cm^{-1}. The hydrogen content of these films was determined by calculating the integrated absorption of local vibration wagging modes of Si-H, Ge-H mono-hydrogen bonds at the peak positions of about 640 cm^{-1} and 570 cm^{-1}, respectively [6, 7, 8].

For SAXS measurement, a duplicate set of films was deposited on high-purity aluminum-foil with conditions similar to those in Table 1. The total integrated SAXS intensity, Q_T, is a good measure of the overall film heterogeneity. The SAXS technique and analysis methods are described elsewhere [11]. The SIMS measurement was also taken on the films deposited on c-Si substrate by using a Cameca IMS-5F instrument to determinate the Ge solid-phase fraction (x) in the films [12].

RESULTS AND DISCUSSION

Between wavenumbers 1700 and 2100 cm^{-1} on each set of FTIR spectra, there are stretch modes of mono-hydrogen bonds of Si-H and Ge-H corresponding to the peaks at approximately 2000 and 1880 cm^{-1}, respectively, and di-hydrogen bonds of Si-H_2 and Ge-H_2 corresponding to the peaks at 2090 and 1980 cm^{-1}, respectively. Superpositions of Gaussians were used to fit these peaks. Figures 1-a and 1-b show these peak fittings for the two sets of films in their stretch band regions. We found no evidence that poly-hydrides of germanium were incorporated in these films; otherwise there would be additional peaks at 830 and 760 cm^{-1} corresponding to the bending modes of polyhydrides of germanium $(GeH_2)_n$ [9, 10], analogous to the two peaks at 890 and 845 cm^{-1}, which are a scissors mode corresponding to the bending modes of polyhydrides of silicon $(SiH_2)_n$. Table 2 lists the results of the various measurements made on these samples listed in Table 1.

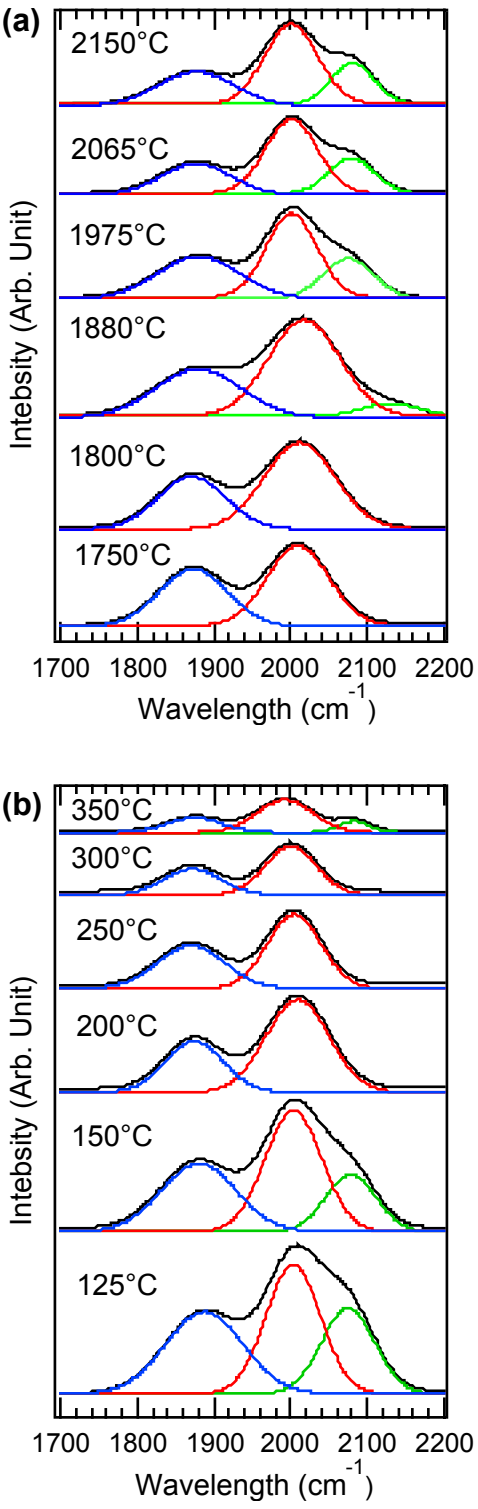

Fig. 1 Three-Gaussians fit to Si-H, Ge-H, and Si-H_2 bonding on the samples deposited under varying T_f (Fig. 1-a) and T_s (Fig. 1-b).

The effects of varying filament temperature

Figure 2 shows that the deposition rate (D. R.), E04, and hydrogen content (C_H) all monotonically decreased as T_f decreased from 2150° to 1750°C. The C_H in the films is relatively constant for this set (12-15 at.%) due to the fixed T_s, but a sharp decrease of D.R. can be seen from about 10 Å/s to 1 Å/s. This demonstrates that the D.R. is mainly dependent on the filament energy under the same deposition pressure. E04 also decreased from 1.54 to 1.41 eV with decrease of T_f. We observed that higher T_f, resulted in higher deposition rates but due to the fixed low T_s at 180°C, the films are porous due to higher fraction of microvoids that usually coexist with polyhydrides of silicon- $(SiH_2)_n$. As can be seen, when T_f is above 1900°C, there is a significant amount (~20% of C_H) of Si-H_2 in the film (Fig. 3), but below 1900°C, the films improved rapidly as demonstrated by the decrease in Si-H_2 and increase in photoconductivity (Fig. 3). The relative amount of Ge-H bonding (to total H-bonding) increases monotonically with decreasing T_f (Fig. 3). This is an additional reflection of the improvement in film quality with decreasing T_f as Ge-H bonding

reflects favorable hydrogen passivation of Ge dangling bonds.

Table 2. Results of the Various Measurements Made on Samples Listed in Table 1.

Sample (Set 1&2)	σ_{photo} ($cm^{-1}.\Omega^{-1}$)	Ratio $\sigma_{photo}/\sigma_{dark}$	E04 (eV)	E_{Tauc} (eV)	n ($633nm^{-1}$)	x (%)	Q_T (10^{24} eu/cm^3)
L902	2.39e-07	356	1.54	1.33	4.511	57.4	20.1
L904	2.80e-07	800	1.54	1.33	4.504	57.4	18.3
L905	3.56e-07	983	1.53	1.32	4.512	60.5	9.92
L907	7.51e-07	736	1.50	1.30	4.685	NA	7.24
L911	6.11e-06	382	1.45	1.26	4.783	66.3	2.61
L913	5.11e-06	203	1.41	1.21	5.054	70.3	1.89
L908	3.53e-07	1	1.40	1.21	4.833	59.7	9.91
L894	8.93e-07	48	1.43	1.23	4.875	61.3	4.58
L895	1.95e-06	179	1.45	1.26	4.875	63.4	2.18
L896	2.10e-06	346	1.47	1.28	4.985	64.6	2.72
L897	8.25e-07	292	1.49	1.29	4.691	64.5	7.11
L898	9.65e-07	283	1.50	1.31	4.711	68.7	10.7

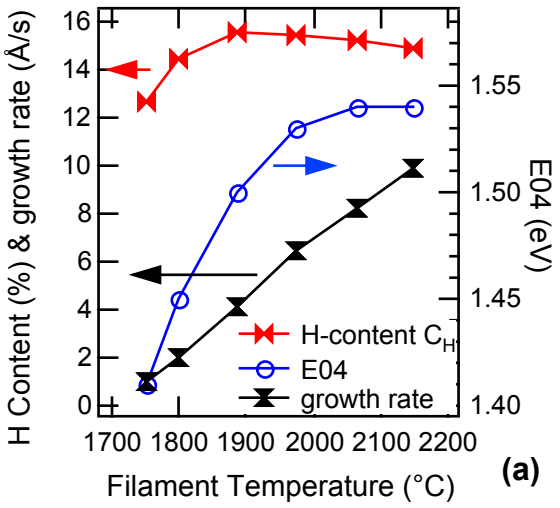

Fig. 2. Variation of deposition rate, E04, and hydrogen content as a function of T_f.

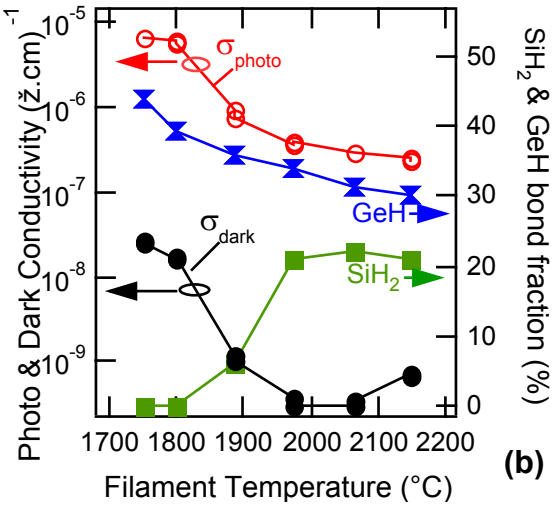

Fig. 3. The effects of T_f on σ_{photo}, σ_{dark}, and Ge-H, Si-H_2 bonding fractions.

The total integrated SAXS intensity decreases monotonically with decreasing T_f, whereas the Ge solid-phase fraction x increases (Fig. 4). This inverse correlation is somewhat surprising, yet may be explained by the fact that the films with higher Ge are grown at lower deposition rates, and thus have improved microstructure.

The higher Ge at lower T_f is due to the lower dissociation energy for GeH_4 relative to SiH_4. The decrease in E04 with decreasing T_f (Fig. 2), is due primarily to the increase in Ge solid fraction (Fig. 4), but also to improved film homogeneity and compactness due to significant reduction of microvoids indicated by the SAXS measurements (Fig. 4).

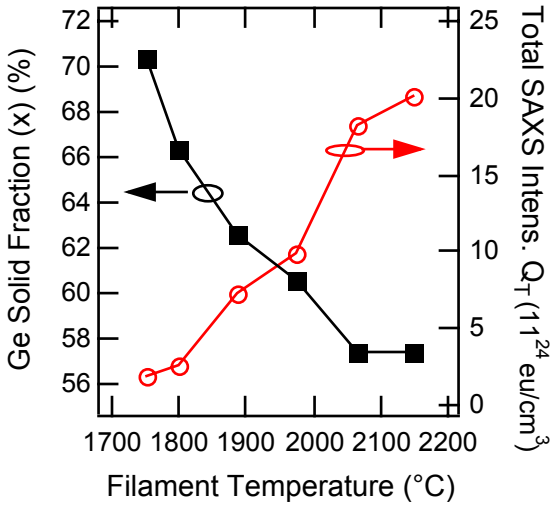

Fig. 4. Increase of Ge fraction x and decrease of total SAXS intensity Q_T with decrease of T_f.

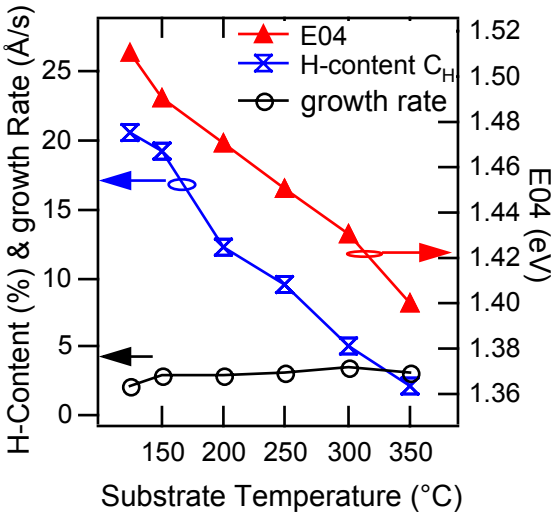

Fig. 5. Variation of deposition rate, E04, and hydrogen content as a function of T_f.

The effects of varying substrate temperature

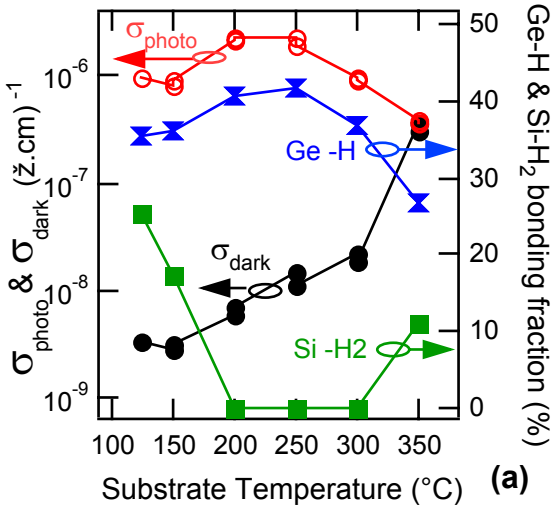

Fig. 6. The effects of T_s on σ_{photo}, σ_{dark}, and Ge-H, Si-H_2 bonding fractions.

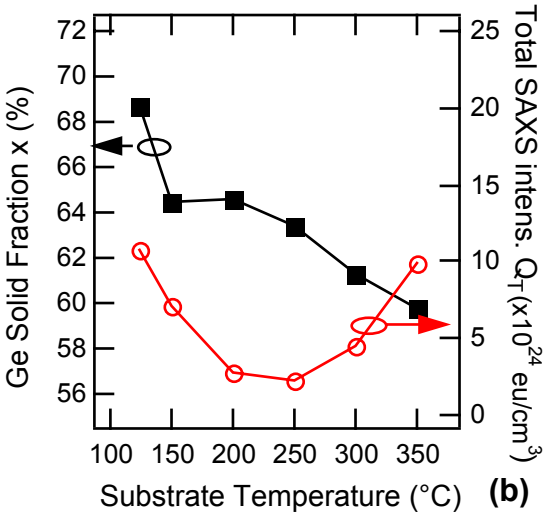

Fig. 7. Smaller increase of Ge fraction x and decrease of total SAXS intensity Q_T at the T_s of 200°-250°C.

In Fig 5, we show that both E04 and C_H are dependent on T_s, whereas the growth rate is not strongly affected by Ts, remaining ~ 2-4 Å/s. When T_s is between 200°- 300°C, Si-H_2 is below the detection limit of FTIR, which is accompanied by increased photoconductivity (Fig. 6).

The total hydrogen C_H in the films increases monotonically from ~2% to ~20% as the T_s is lowered from 350° to 125°C. This large change in C_H has a strong influence on E04, which increases from 1.4 to 1.5 eV with the same decrease of T_s. The relative amount of Ge-H bonding is a maximum in the optimized temperature range of 200°- 300°C, which correlates nicely with

higher photoconductivity (Fig. 6). The lowering of T_s has a profound improvement (lowering) of the dark conductivity (Fig. 6).

The total integrated SAXS intensity is a minimum in the optimized temperature range of 200°- 300°C, whereas Ge increases monotonically with decreasing T_f (Fig. 7). The improvement of optoelectronic properties in this optimized T_s range correlates nicely with the SAXS intensity, even though there is a small increase of Ge fraction x (Fig. 7).

CONCLUSIONS

Based on above evidence, lowering T_f (<1850°C) and optimizing T_s (200°-250°C) can improve the structural and optoelectronic properties of narrow-gap a-SiGe:H alloys deposited by HWCVD, in which a 0.38-mm tungsten wire was used, resulting in a D.R. of about 3Å/s. The improved material has about 65% Ge, an optical band gap around 1.3 eV, and an activation energy about 0.64 eV. This material has a C_H of about 10%, with over 40% of Ge-H bonding and about 60% of Si-H bonding but without detectable di-hydride bonding ($Si-H_2$, $Ge-H_2$). Therefore, this material has higher photoconductivity (~ 10^{-6}) and photosensitivity (about 200-500). This material has much improved homogeneity as measured by SAXS, compared to all other such alloys with high Ge content.

ACKNOWLEDGMENT

This work was performed under DOE contract number DE-AC36-99GO10337.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 2003	Conference Paper

4. TITLE AND SUBTITLE
Influence of Filament and Substrate Temperatures on Structural and Optoelectronic Properties of Narrow Gap a-SiGe:H Alloys Deposited by Hot-Wire CVD: Preprint

5. FUNDING NUMBERS
PVP34101

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
NREL/CP-520-33936

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words):*
We have found that narrow-bandgap—1.25 < Tauc Gap < 1.50 eV—amorphous silicon germanium (a-SiGe:H) alloys grown by hot-wire chemical vapor deposition (CVD) can be improved by lowering both substrate and filament temperatures. We systematically studied films deposited using a one-tungsten filament, decreasing filament temperature (T_f) from our standard temperature of 2150° down to 1750°C, and fixing all other deposition parameters. By decreasing T_f at the fixed substrate temperature (T_s) of 180°C, the Ge-H bonding increases, whereas the Si-H_2 bonding is eliminated. Films with higher Ge-H bonding and less Si-H_2 have improved photoconductivity. For the series of films deposited using the same germane gas fraction at 35%, the energy where the optical absorption is $1x10^4$ (E04) drops from 1.54 to 1.41 eV with decreasing T_f. This is mainly due to the combination of an increasing Ge solid fraction (x) in the film, and an improved homogeneity and compactness due to significant reduction of microvoids, which was confirmed by small-angle X-ray scattering (SAXS). We also studied a series of films grown by decreasing the T_s from our previous standard temperature of 350°C down to 125°C, fixing all other deposition parameters including T_f at 1800°C. By decreasing T_s, both the total hydrogen content and the Ge-H bonding increased, but the Si-H_2 bonding is not measurable in the T_s range of 180°-300°C. The E04 increases from 1.40 to 1.51 eV as T_s decreased from 350° to 125°C, mainly due to the increased total hydrogen content. At the same time, the photo-to-dark conductivity ratio increases almost three orders of magnitude over this range of T_s.

14. SUBJECT TERMS: PV; amorphous silicon germanium; hot-wire chemical vapor deposition; narrow bandgap; tandem solar cells; X-ray scattering (SAXS); photoconductivity; photosensitivity; optoelectronic;

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL